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## NO DRAWINGS

(21) Application No. 44038/67 (22) Filed 27 Sept. 1967

(23) Complete Specification filed 13 Sept. 1968

(45) Complete Specification published 15 Sept. 1971

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(72) Inventor ERIC MARIA BRINCKMAN



(54) IMPROVEMENTS RELATING TO THERMO-RECORDING

5

## ERRATUM

SPECIFICATION No. 1,245,924

Page 1, lines 1 and 2, for "naamloze vennoot-  
schap" read "Naamloze Vennootschap"

THE PATENT OFFICE  
15th February 1972

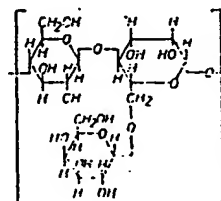
21

in contact with the recording material so that heat is conducted from such markings to the recording layer. Depending on the kind of change brought about in the recording layer, the information-wise heating results in a visible record or a latent record which has to be developed to a visible form by application of a developing substance, e.g., a powder which adheres to the areas of the recording layer which have been transformed by heating, or a liquid which removes those areas of the recording layer or the background areas.

The present invention provides heat-sensitive recording materials with very good properties for use in forming, by information-wise heating, a latent record which is accompanied by an information-wise change in the solubility of the recording layer and can thus be developed by development techniques based on the treatment of the recording material with a solvent. The invention also comprises recording methods using such materials.

According to the present invention, there is provided an information-recording method

[Price 25p]



(2) a hydroxypropylmethylcellulose (preferably having a degree of substitution of 1.7—1.8 (methyl) and 0.1—0.2 (hydroxypropoxyl) and a viscosity such that a 2% solution in water at 20°C has a viscosity of 45 Poises);

(3) a slightly hardened methylol melamine resin or a slightly hardened wholly or partially etherified methylol melamine resin of the water-soluble type, e.g. a methylated methylol melamine resin (such resin having preferably been slightly hardened by the addition of an inorganic or organic compound containing acidic groups, by moderately

SEE ERRATA SLIP ATTACHED

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 (72) Inventor ERIC MARIA BRINCKMAN



## (54) IMPROVEMENTS RELATING TO THERMO-RECORDING

(71) We, AGFA-GEVAERT, a naamloze vennootschap organised under the Laws of Belgium, formerly Gevaert-Agfa, a Belgian Company, of 27, Septestraat, Mortsel-Antwerp, Belgium, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a method of recording information by means of a heat-sensitive recording material.

Various heat-sensitive recording materials have been proposed for use in recording graphic information. Such materials comprise a recording layer which undergoes some physical and/or chemical change when heated. Normally such materials are intended to be information-wise heated by generating heat by means of radiant heat energy in image markings of a graphic original while this is in contact with the recording material so that heat is conducted from such markings to the recording layer. Depending on the kind of change brought about in the recording layer, the information-wise heating results in a visible record or a latent record which has to be developed to a visible form by application of a developing substance, e.g., a powder which adheres to the areas of the recording layer which have been transformed by heating, or a liquid which removes those areas of the recording layer or the background areas.

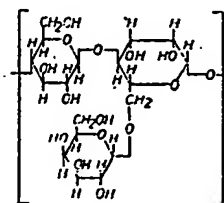
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According to the present invention, there is provided an information-recording method

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wherein a recording material is used comprising a heat-sensitive recording layer of a composition such that the solubility of any given area of the layer in a given solvent (to be used in the method) can be increased by heating that area of the layer, wherein the said layer is information-wise heated to produce a record of the information in terms of a difference in the solubilities in the said solvent of different areas of the recording layer, and wherein the whole layer is then contacted with such solvent to cause the portions of the recording layer which are soluble or most soluble in such solvent to be removed or penetrated by such solvent, the said method being characterised in that the said recording layer is wholly or mainly composed of one or more heat-sensitive polymeric compounds or compositions identified in the following list:

(1) a galactomannan, which is a glucoside having the following structural units:



(2) a hydroxypropylmethylcellulose (preferably having a degree of substitution of 1.7—1.8 (methyl) and 0.1—0.2 (hydroxypropexyl) and a viscosity such that a 2% solution in water at 20°C has a viscosity of 45 Poises);

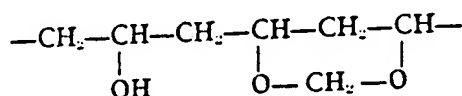
(3) a slightly hardened methylol melamine resin or a slightly hardened wholly or partially etherified methylol melamine resin of the water-soluble type, e.g. a methylated methylol melamine resin (such resin having preferably been slightly hardened by the addition of an inorganic or organic compound containing acidic groups, by moderately

SEE ERRATA SLIP ATTACHED

all-over heating the recording layer, or simply by keeping the recording material at room temperature for some weeks). Suitable additives containing acidic groups are, e.g., citric acid, ascorbic acid, boric acid, malic acid, anhydride, phosphoric acid, gallic acid, barbituric acid, 2,4-dihydroxy-benzoic acid, p-amino-salicylic acid, stearic acid, itaconic acid, mandelic acid, succinic acid, methacrylic acid and polyacrylic acid;

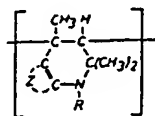
(4) a resorcinol formaldehyde resin which is soluble in ethanol or in a mixture of ethanol and water and which becomes soluble in water alone by heating;

(5) a composition containing a water-soluble polyvinyl alcohol mixed with a compound containing (a) reactive carbonyl group(s) e.g. formaldehyde or 1,4-dichloro-2,3-butanedione. (The reaction with formaldehyde probably results in the formation of an acetal grouping of the following type:



An essential condition for obtaining a product that is soluble in water is the use of formaldehyde in an amount that is considerably smaller than that of the polyvinylalcohol);

(6) a composition which becomes water-soluble or more water-soluble on heating and comprises an acidic compound and a water-insoluble polymer containing a basic nitrogen-containing heterocyclic nucleus of the type present in the following recurring unit:



wherein:

Z represents the necessary atoms to complete a substituted or unsubstituted aromatic nucleus, and

R represents hydrogen or a group which maintains the basic properties of the nitrogen atom to which it is attached, e.g., an aliphatic hydrocarbon group or substituted aliphatic hydrocarbon group such as an alkyl group or aralkyl group, more particularly a methyl or benzyl group. (Said acidic compound is preferably hydrochloric acid, acetic acid, or a polymer or a copolymer of an  $\alpha,\beta$ -ethylenically unsaturated compound containing a carboxylic or sulphonic acid group, e.g., polyacrylic acid, polystyrene sulphonic acid, copoly(methacrylic acid/styrene), copolyacrylic acid/N-vinylpyrrolidone), copolyacrylic acid/acrylamide), copoly(methacrylic acid/methylmethacrylate), methacrylic acid,

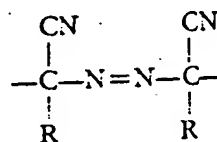
or an analogous compound. The acidic compound is preferably used in a weight ratio of 20—400% in respect of the basic polymer, more preferably in a weight ratio of 50 to 300%. Said basic polymer is preferably poly-(1,2-dihydro-2,2,4-trimethylquinoline);

(7) a reaction product of (a) a water-soluble polymer or copolymer of an  $\alpha,\beta$ -ethylenically unsaturated compound containing one or more carboxylic acid groups, e.g. polyacrylic acid, and (b) a reactive compound such product being one which is less soluble in water than said polymeric compound but which on being heated dissociates to form a composition which is more soluble in water than said reaction product. (Suitable reactive compounds are cobalt naphthenate and 2,4-dihydroxy benzophenone);

(8) a cresol-formaldehyde resin of the novolak type, which resin can advantageously be mixed with a peroxide compound, e.g. cumene hydroperoxide;

(9) a phenol-formaldehyde resin of the novolak type, which resin can advantageously be mixed with a peroxide compound, e.g. cumene hydroperoxide. The novolak resins are prepared in a manner similar to that used for the preparation of resole resins save for the fact that the reaction is conducted in an acidic medium, instead of an alkaline medium as is the case with resoles. In a typical synthesis novolaks are prepared by heating one mole of the phenol or cresol with 1 to 0.5 mole of formaldehyde in an acidic medium. The temperature at which the reaction is conducted is generally from about 25°C to about 175°C).

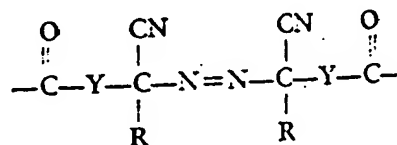
(10) a polymer (which may be a homocopolymer) containing an azo group linked through a carbon atom to a nitrile group. Preferred polymers in this category are polymers comprising groups of the following structure:



wherein:

R represents a lower alkyl group ( $\text{C}_1-\text{C}_3$ ), preferably a methyl group.

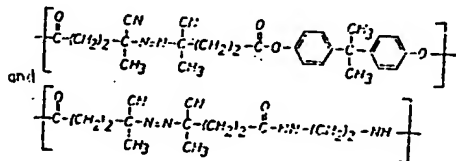
The preparation of polymers containing such groups is described in "Die Makromolekulare Chemie", 103 (1967) p. 301—303. Typical representatives are polyesters and polyamides containing the following structural group in their recurring units:



wherein:

R represents a lower alkyl group and Y a bivalent hydrocarbon radical preferably an alkylene radical of less than 4 carbon atoms.

Particularly good results are obtained with a polyester or a polyamide having the following recurring units respectively:



- (11) poly-N-vinylpyrrolidone;
  - (12) crude and/or bleached shellac which can advantageously be mixed with a peroxide compound, e.g., cumene hydroperoxide;
  - (13) poly(1,2 - dihydro - 2,2,4 - trimethylquinoline);
  - (14) poly-N-vinylpyrrolidone in admixture with a water-soluble melamine-formaldehyde resin;
  - (15) a composition containing polyvinyl alcohol or a partially hydrolyzed polyvinyl acetate mainly containing vinyl alcohol units, mixed with a quinone-diazide compound (e.g., as described in United Kingdom Patent Specification No. 1,136,544) and an aldehyde or a latent aldehyde, preferably formaldehyde, or a latent aldehyde splitting off formaldehyde on heating, e.g. dimethylolurea. As suitable quinone-diazide compounds are particularly mentioned: naphthoquinone - 1,2-diazide(2) - 5 - sulphonylchloride and naphthoquinone - 1,2 - diazide(2) - 4-sulphonylchloride;
  - (16) a copoly(styrene/N-vinylpyrrolidone) which has been used as a latex (aqueous dispersion) in forming the recording layer and which undergoes an increase in solubility in a C<sub>1</sub>-C<sub>2</sub> alkane on being heated;
  - (17) a copoly(styrene / acrylate ester) which has been used as a latex, in forming the recording layer and which undergoes an increase in solubility in acetone on being heated. Preferably the polymer is copoly-(styrene/ethyl acrylate) (20/80);
  - (18) a composition containing a copoly-(butadiene/styrene) and an ortho-quinone-diazide compound, e.g., a compound of that kind as described in United Kingdom Patent Specification No. 1,116,737 such as 2,2-bis(2 - bromo - 6 - diazo - 2,4 - cyclohexadiene - 4 - yl - 1 - one) - propane, or an ortho-quinone-diazide compound splitting off an acid on heating as described in United Kingdom Patent Specification No. 1,140,524.
- The solvent applied to the recording material after the image-wise heating may

comprise a single compound or a mixture of compounds.

The solvent used in the method has to be selected appropriately for the selected heat-sensitive compound or composition. A simple heating test on a given compound or composition, e.g., in a test tube, followed by a treatment with a liquid that is not a solvent for the unheated compound or composition suffices to show whether the compound or composition exhibits the necessary increase in solubility in that particular solvent.

The compounds and compositions (1) to (7) show an increase in water-solubility on being heated; compounds (8) to (12) show an increase in solubility in an alkaline aqueous medium, e.g., an aqueous solution having a pH 12 whereas compounds (14) also shows an increase in solubility in an ether-type solvent, e.g., ethyl glycol or methyldiethylene-glycol; compounds (12) to (16) show a rise in solubility in a C<sub>1</sub>-C<sub>2</sub> alkane, e.g., ethanol; compounds (16) and (17) show a rise in solubility in an organic carbonyl compound containing two C<sub>1</sub>-C<sub>1</sub> alkyl groups linked to the carbonyl group, e.g., acetone, and composition (18) shows an increase in solubility in chlorinated aliphatic hydrocarbons, e.g., methylene chloride and carbon tetrachloride.

Up till now the best results have been obtained with the compositions 3, 6, 8 and 9.

In the case that the soluble or most soluble portions of the recording layer are removed in the solvent treatment step a relief record remains on the recording material. According to preferred embodiments of the invention the recording layer is black or coloured and after the information-wise heating of the recording layer the soluble or the most soluble portions are removed by the solvent treatment so as to leave a visible black or coloured image. When using this developing technique the dye or pigment used for colouring the recording layer should preferably be insoluble in the solvent medium used so as to be resistant to diffusion.

In the case that the recording layer composition is such that it is to some degree permeable by the selected solvent even before transformation by heating, the treatment with the solvent may be such that the solvent removes the portions which have become more soluble by being heated and penetrates into but does not actually remove the other portions of the layer. In that case, the recording layer may be colourless and the solvent medium may be coloured so as to colour or to change the colour of such other portions of the recording layer.

The above definition of the invention shows however that the invention is not restricted to methods wherein the solvent treatment removes the soluble or the most soluble

portions of the recording layer but also includes methods wherein the solvent used is allowed merely to penetrate into such portions. By such penetration, various results can be achieved. Thus, once the said portions have become penetrated by solvent they can be transferred by adhesion to a receptor sheet by temporarily pressing such sheet into contact with the recording layer while it is wet and peeling the recording material and receptor sheet apart. If the solvent medium is coloured, so as to colour or to confer a different colour on the portions of the recording layer into which the medium penetrates, then the treatment with the solvent is all that is required to produce a copy. If the recording layer is a coloured layer then the solvent medium employed may be composed so as to discolour or bleach the recording layer in the portions thereof into which the medium penetrates, or the solvent medium may be used to enable colouring matter to diffuse from the recording layer onto a receptor sheet to form a visible record thereon. In the latter case the colouring matter can be a dye which can be used in spirit duplicating so that the receptor sheet bearing the transfer image can be used a spirit duplicating master. Of course there are many other development possibilities. For example, a solvent medium may be used which contains a compound which enters into a colour-forming reaction with a compound present in the recording layer, or a solvent medium may be used which contains a catalyst for initiating a colour-forming reaction between reactants already present in the recording layer.

In the case that the information to be recorded is in the form of a printed document, normally some areas of the recording layer will be heated while the other areas are substantially unheated. However the invention can be used for copying a continuous tone graphic original such that in the information-wise heating step the whole recording layer is heated but different areas are heated to different extents. In other words, the recording layer is information-wise differentially heated. For convenience reference is primarily made herein to heated and unheated portions.

In order to make the recording layer sufficiently insoluble in the processing liquid, e.g., water, before the image-wise heating, it is sometimes necessary, e.g., in the case of the above-mentioned melamine resins to heat the recording layer after its formation for a certain time at a temperature between 50 and 130°C, e.g., for 5 hours at 80°C or for 5 minutes at 120°C. The appropriate processing time and temperature should be determined experimentally, since too strong and too lengthy a heating causes an insolubility in water, which cannot be reversed by a rather short-high-intensity heating.

The recording layer, which may be a self-

supporting layer, (i.e., a sheet) or a layer carried by a suitable support, can incorporate various types of ingredients in addition to one or more of the heat-sensitive compounds or compositions hereinbefore listed. The further ingredient or ingredients (if any) can be selected so as to permit or promote the required processing step, using the liquid solvent medium, to be performed after the information-wise exposure of the recording layer. For example the recording layer may incorporate a dye or pigment, (which may be a dye or pigment which will diffuse out of the layer or which will resist diffusion out of the layer, in the solvent medium), electro-conductive particles, e.g., carbon particles or metal particles, reaction components for the formation of a dye and/or a catalysts for including a colour reaction a light-sensitive substance, e.g., light-sensitive silver halide, a silver-halide developing substance, and/or developing nuclei for complexed silver halide salts. The recording layer may also contain reinforcing or filling agents and small inert inorganic particles, e.g. particles of glass, mica, or silica or bentonite. Preferably these ingredients are used in a weight ratio in respect of the selected heat-sensitive polymer(s) not exceeding 20%.

With a view to facilitating the eventual removal of heated portions of the recording layer in an aqueous liquid, the layer may be formed from a composition incorporating one or more water-soluble compounds into this layer in an amount as not substantially to disturb the selectivity of the washing away with such aqueous liquid, e.g., polyacrylic acid, polyacrylamide, poly-N-vinylpyrrolidone and polyoxethylene resins.

In an analogous manner the washing away of the heated portions of recording layers that are not removable with an aqueous liquid can be improved by incorporating in the recording layer compounds which have a good solubility in an organic solvent to be used in development processing.

The methods and materials according to the invention are intended primarily for reproduction of graphic originals e.g. line or halftone originals, but the invention is nevertheless capable of wider application e.g. for recording data applied as a heat pattern to the recording material responsive to transmitted signals.

In the performance of the invention for copying a graphic original, the information-wise heating of the recording layer may be brought about by heating the image markings of the original while these are in heat-conductive relation with the recording layer. If the image markings are infra-red absorbing such heating may be performed by exposing the original to infrared radiation. If the image-markings are sufficiently light-absorb-

ing, such heating may be brought about by exposing the original to visible light.

The exposure of the graphic original to the radiation to be absorbed by the image markings may take place while such markings are in contact with the recording layer. In the case of a typewritten document, this results in a laterally reversed latent image in the recording layer. If the recording layer is carried by a transparent support and the latent image is developed by washing away the most soluble portions of the recording layer and, if required colouring the remaining portions, an image is obtained, which is legible through the transparent support.

If the recording layer contains dyes or reactive components soluble in a suitable printing liquid, the thus developed recording material can be used as a master from which it is possible to obtain legible prints on a suitable receiving material, e.g., it can be used as a matrix for spirit duplicating.

According to another embodiment the heat-sensitive layer is placed against the back or unprinted surface of a document during irradiation. The heat absorbed in the image markings is conducted through the backing towards the heat-sensitive layer. This "back-printing" method makes possible the production of a legible copy if the original is printed on a sufficiently thin, heat-resistant, heat-conductive base of paper or other material.

According to preferred embodiments of the invention, the recording material contains one or more substances which are capable of absorbing electromagnetic radiation to be used in exposing the recording material so that the heat required for information-wise changing the recording layer in respect of its solubility can be generated within the recording material itself. In such embodiments visible light and infra-red light are preferably used, but ultraviolet light and other energetic electromagnetic radiation can be used if it is sufficiently absorbed by the recording material to give rise to the necessary heating.

Some specific examples of substances absorbing visible light and infrared radiation, which can be incorporated in the recording material and which are preferably present in the recording layer to provide an optical density for the copying light of at least 0.25 are finely divided carbon particles, e.g., carbon black, and heavy metals in finely divided state, e.g., silver, bismuth, lead, iron, cobalt, and nickel, oxides and sulphides of these metals, e.g., manganese dioxide, magnetic iron oxide ( $\text{Fe}_3\text{O}_4$ ), chromium oxide ( $\text{CrO}$ ), cobalt sulphide, nickel sulphide, lead sulphide, and pigments and dyes such as Prussian blue and indigo. The particle size of these substances preferably does not exceed 0.1 microns. These light-absorbing substances can be incorporated in the heat-

sensitive layer or in an adjacent layer providing that a heat-conductive relationship with the thermosensitive polymeric compound or composition exists. When carrying out the exposure of the recording material it is necessary to ensure that there is no or insufficient heat transfer from the graphic original (if such is used) to cause the recording layer to be heated non-differentially over its whole area.

Methods and apparatus, by which, using the heat-generating property of said substances, the recording material can be exposed to an original are described in United Kingdom Patent Specifications Nos. 1,160,221, 1,139,891 and 1,154,902.

In recording an original according to a preferred embodiment of the invention, the recording layer of the recording material is of such composition that it becomes soluble or more soluble in water on being heated and incorporates electromagnetic radiation-absorbing substance(s) for heat production in the recording layer and the material is subjected to a short duration high intensity image-wise exposure to visible light and/or and/or infra-red radiation which is transmitted by or reflected from the background areas of a graphic original located in contact with the recording material. The image markings of the original may be in heat-conductive relationship with the heat-sensitive recording layer, if the exposure is an exposure to high intensity radiation for a brief period of time. The exposure time preferably does not exceed  $10^{-1}$  second. In such very short exposure periods there is insufficient heat conduction to the recording layer from the image markings to have any significant effect on the solubility of the recording layer. On the other hand the radiation absorbing substance(s) in the recording layer absorb(s) radiation and heat is generated in the surrounding heat-sensitive compound or composition sufficiently to bring about the required image-wise solubility differentiation.

The short duration exposure may be performed by using a flash lamp preferably supplying a light energy of 100 to 1000 Watt-seconds in a time interval of  $10^{-2}$  to  $10^{-3}$  seconds. The intensity of the exposure which must be used depends on the composition of the recording layer. Normally an exposure energy of at least 0.1 Wattseconds/cm<sup>2</sup> is employed for obtaining a sufficient solubility differentiation.

Gas discharge lamps with a much lower energy output can be used, of course, if the emitted energy is focussed onto a relatively small area of the recording material. Obviously, the successive exposure may be carried out progressively, in other words by exposing adjacent areas of the recording layer. The exposure is not necessarily a continuous



one but can be executed by an intermittent flashing.

For suitable developing techniques based on the difference in water-permeability and swellability in water reference is made to United Kingdom Patent Specifications Nos. 1,139,891 and 1,160,221.

The present invention is mainly intended for obtaining a copy of a printed text, line drawings, or screened original by washing away the heated portions of a recording layer which contains a coloured pigment. If the recording layer is carried on a screen support, e.g. a nylon gauze, Japan paper, or metal wire screen, a screen printing master is obtained by selectively washing away the recording layer. Although the removal of the heated portions of the recording layer according to a preferred embodiment is carried out with a pure solvent or solvent mixture in the case no alkali is needed, the development can also be carried out with solvent compositions containing a minor proportion, preferably less than 20% by weight, of dissolved substances e.g. wetting agents or detergents, for improving the selective removal of the heated portions of the recording layer. The same substances can enable the developer composition simultaneously to penetrate into the non-heated portions of the recording layer and such composition may contain a colouring substance, e.g. a dye, dye forming component(s) or (a) catalyst(s) for a dye forming reaction.

When choosing a suitable support and an appropriate thickness of the recording layer the relief image left after washing away the heated portions of the recording layer can be used for planographic printing (relief not very pronounced) or letterpress printing (pronounced relief). In planographic printing the relief portions or portions of the support or subjacent layer can act as the printing portions. Printing is possible with a lipophilic ink as well as with a hydrophilic ink depending on the composition of the recording layer or the subjacent layer or support. A planographic printing process wherein use is made of a hydrophilic ink is called "reversed planographic printing". For such a process and suitable inks reference is made to United Kingdom Patent Specification No. 1,142,472.

When letterpress printing reliefs are being prepared an after-hardening of the relief portions or application thereto of lacquer may be necessary. If desired the support carrying the relief portions can be etched in the non-shielded portions and the resist image can then be removed preparatory to carrying out relief or intaglio printing.

In the preparation of letterpress printing reliefs the original is preferably an image-bearing transparency consisting solely of substantially opaque and substantially transparent

areas, the opaque areas being of the same optical density, i.e., a so-called line or half-tone negative. Both negative or positive transparencies can be used as originals. Since light is passed essentially only through the clear areas in the transparency, only the areas of the thermosensitive layer which correspond with such clear areas are heated by absorption of radiation and become more soluble. The image of the clear areas of the transparency that is produced in the polymer layer or sheet, after removal of the portions with increased solubility, is intaglio. These recessed areas constitute the non-printing portions, of a letterpress plate. The ink-carrying portions, i.e. the printing relief, in such plates are those portions which were under the opaque area of the transparency and accordingly were not increased in solubility. In general, a positive transparency is used when the usual photoengraving procedure would employ a negative, and vice-versa.

Depending on the type of polymer, the ingredients associated therewith and the intensity of heating, the increase in solubility by heating can be due to depolymerization, hydrolyzation, degradation, or transformation from non-polar (non-ionicless water-soluble) to more polar (ionic—more water-soluble) character of the polymer.

The following examples illustrate the present invention without, however, limiting it thereto.

#### EXAMPLE 1

A subbed cellulose triacetate film was coated with the following dispersion:

hydrolysed polyvinyl acetate having from 97.5—99.5% of acetyl groups replaced by hydrolysis (the viscosity at 20°C of a 4% aqueous solution is 5 cps)	25 g	
20% aqueous solution of formaldehyde	25 ccs	
aqueous carbon black dispersion containing per 100 g: 53 g of carbon (particle size less than 0.1 micron), 23 g of water, 18 g of ethylene glycol and 6 g of nonylphenyl polyethylene oxide	1 g	
water	250 ccs	

The recording material was exposed through a half-tone transparency by means of a flash lamp having an exposure time of  $8 \cdot 10^{-3}$  second and irradiating the material with an energy of 1.03 Wattsecond/cm<sup>2</sup>. The recording material was then rinsed in running water for 3 minutes, whereby only the exposed portions of the recording layer were washed away. A positive black copy of the original was obtained.

After drying of the coated layer, the optical density (measured by transmission) of the recording material was 0.34.

#### EXAMPLE 2

- 5 A subbed cellulose triacetate film was coated with the following dispersion:

10	a 80% by weight aqueous dispersion of PAREZ RESIN 6 B (a dimethyltrimethylol-melamine-formaldehyde resin sold by American Cyanamid Company, New York, N.Y., U.S.A.)	44 g
	carbon black dispersion as used in Example 1	1 g
15	water	80 ccs

- 20 After drying of the coated layer for 1 hour at 80°C, the optical density (measured by transmission) of the recording material was 0.26.

The recording material was reflex-exposed while in contact with an opaque line original by means of an electronic flash-lamp irradiating the recording material with an energy of 1.01 Wattsecond/cm<sup>2</sup>.

- 25 The recording layer was then rubbed with a plug of wadding soaked with water. A black positive copy of the original was visible through the transparent cellulose triacetate support.

#### EXAMPLE 3

A subbed cellulose triacetate film was coated with a dispersion consisting of:

35	poly(1,2 - dihydro - 2,2,4-trimethylquinoline) sold by Monsanto Chemical Company, St. Louis, Mo., U.S.A., under the trade mark FLECTOL H	5 g
	polyacrylic acid	6 g
40	ethanol	95 ccs
	carbon black dispersion as used in Example 1	4 g

- 45 After drying of the coated layer, the optical density (measured by transmission) of the recording material was 2.63. The exposure was the same as described in Example 1. The exposed portions of the recording layer were selectively removed by rubbing with a plug of wadding soaked with water.

- 50 A positive black copy of the original was obtained.

#### EXAMPLE 4

A subbed cellulose triacetate film was coated with a dispersion consisting of:

water	120 ccs	55
60% neutral solution of a cold-hardenable resorcinol - formaldehyde resin in a mixture of equal parts of ethanol and water (viscosity at 20°C: 300 cps)	44 ccs	60
Aqueous carbon dispersion as described in Example 1	1 g	

After having been dried the material had an optical density (measured by transmission) of 0.80.

The material was exposed as described in Example 1. The exposed areas were removed by washing with water. A black positive image was obtained.

#### EXAMPLE 5

A subbed cellulose triacetate film was coated with a dispersion consisting of:

water	65 ccs	75
1% aqueous solution of a galactomannan	42 ccs	
aqueous carbon dispersion as described in Example 1	1 g	
11.5% aqueous solution of saponine	1 cc	80

After having been dried, this material had an optical density (measured by transmission) of 0.64.

The material was exposed as described in Example 1. The exposed areas were removed by holding the material under a vigorous water jet. A black copy was obtained from the original.

#### EXAMPLE 6

A subbed cellulose triacetate film was coated with a dispersion consisting of:

poly(1,2 - dihydro - 2,2,4-trimethylquinoline) (sold by Monsanto Chemical Company, St. Louis, Mo., U.S.A., under the trade mark FLECTOL H)	1 g	95
1% solution of a low molecular weight poly(styrene-p-sulphonic acid) in ethanol	75 g	
aqueous carbon dispersion as described in Example 1	2 g	100

After having been dried, the material had an optical density (measured by transmission) of 1.08.

The material was exposed as described in Example 1. The exposed areas were rubbed away by means of a plug of wadding soaked with water. A black copy was obtained from the original.

## EXAMPLE 7

A subbed polyethylene terephthalate film was coated with a dispersion consisting of:

	ethanol	42 ccs
5	poly(1,2 - dihydro - 2,2,4-trimethylquinoline) (sold by Monsanto Chemical Company, St. Louis, Mo., U.S.A., under the trade name FLECTOL H)	2.5 g
10	methacrylic acid	6 g
	carbon dispersion as described in Example 1	2.5 g

After having been dried, the material had an optical density (measured by transmission) of 1.63.

The material was exposed as described in Example 1. The exposed areas were rubbed away by means of a plug of wadding soaked with water. A black copy was obtained from the original.

## EXAMPLE 8

The following ingredients were ball-milled for 6 hours:

	bleached shellac	25 g
25	ethanol	225 ccs
	carbon black (average particle size 0.1 $\mu$ )	1 g

A subbed polyethylene terephthalate support was coated with the resulting dispersion, in such a way that upon drying a heat-sensitive material with an optical density (measured by transmission) of 0.48 was obtained.

The material was then exposed as described in Example 1. The exposed areas were removed by rubbing the material with a plug of wadding soaked with an aqueous 0.6% solution of sodium hydroxide. A black positive copy, which could also be used as a printing plate for offset printing, was obtained.

## EXAMPLE 9

The following ingredients were ball-milled for 3 hours:

45	phenol-formaldehyde resin, type novolak	25 g
	carbon black (average particle size 0.1 $\mu$ )	1 g
	acetone	225 g

The novolak type phenol-formaldehyde resin was prepared according to the following procedure:

20 moles of phenol were mixed with 50 ccs of concentrated hydrochloric acid and heated till the temperature of 85°C was reached. At this temperature 15 moles of formaldehyde from a commercial 30% formalin-solution were added and the reaction

temperature was increased till 100°C. The reaction mixture was kept at that temperature till the smell of formaldehyde had disappeared. The resin formed was washed with water at 90—100°C and from the resinous mass the excess of phenol was removed by vacuum distillation at 170°C/12 mm Hg. The brittle resinous mass left on cooling was powdered in a ball-mill.

A polyethylene terephthalate support was coated with the resulting dispersion in such a way that upon drying the obtained material had an optical density (measured by transmission) of 0.43. The material was reflex exposed as described in Example 2 and rinsed in a 0.6% aqueous solution of sodium hydroxide. A black positive print of the original remained on the film.

## EXAMPLE 10

The following ingredients were ball-milled for 4 hours:

	bleached shellac	25 g
	carbon black (average particle size 0.1 $\mu$ )	1 g
	ethanol	225 ccs
	cumene hydroperoxide	5 g

A copper plate was coated with the resulting dispersion so as to form thereon a heat-sensitive layer, which upon drying was 7  $\mu$  thick. The material was exposed as described in Example 1. The plate was then rinsed in a 1% aqueous solution of sodium hydroxide, whereby the exposed areas were washed away. Subsequently the plate was dipped for 10 min. in a 10% aqueous iron (III) chloride solution and rinsed with pure water, whereupon the still remaining heat-sensitive layer was removed with acetone. An image-wise etched copper plate was obtained.

## EXAMPLE 11

The following ingredients were ball-milled for 6 hours and applied to a subbed polyethylene terephthalate film support:

	poly (N - vinyl pyrrolidone) (average molecular weight 0,000)	12 g
	ethanol	20 ccs
	water	80 ccs
	carbon black (average particle size 0.1 $\mu$ )	0.3 g

The resulting heat-sensitive material had an optical density (measured by transmission) of 0.70 after drying.

The material was exposed as described in Example 1, and rinsed with a 0.5% aqueous solution of sodium hydroxide. A black positive image was obtained.

## EXAMPLE 12

The following ingredients were ball-milled for 12 hours:

5	phenol - formaldehyde resin, type Novolak (prepared analogously to the preparation of Example 9)	10 g
	cobalt(II) sulphide	4 g
	cumene hydroperoxide	0.5 g
10	ethanol	60 ccs

The resulting dispersion was applied to a subbed polyethylene-terephthalate film support in such a way that upon drying the material had an optical density (measured by transmission) of 0.44. After exposure of the material as described in Example 1, the exposed areas were removed by rubbing with a plug of wadding soaked with a 0.6% aqueous solution of sodium hydroxide. A grey positive image was obtained.

## EXAMPLE 13

The following ingredients were ball-milled for 12 hours:

25	bleached shellac	10 g
	manganese dioxide	2 g
	ethanol	60 ccs

The resulting dispersion was applied to a subbed polyethylene terephthalate support, so that upon drying the optical density of the material (measured by transmission) was 0.44. After exposure of the material as described in Example 1, the exposed areas were removed by rubbing with a plug of wadding soaked with a 0.6% aqueous solution of sodium hydroxide. A black positive image was obtained.

## EXAMPLE 14

The following ingredients were ball-milled for 6 hours:

40	ethanol	50 ccs
	cresol - formaldehyde resin, type Novolak (prepared analogously to the preparation of Example 9)	10 g
45	Milori-blue (C.I. Pigment Blue 27)	3 g

The resulting dispersion was applied to a subbed cellulose triacetate support provided with a gelatin layer having a weight of 7 g/sq.m. The thickness of the heat-sensitive layer was 11 microns after drying. The resulting material was exposed as described in Example 1. The exposed portions were removed by dipping in an 0.6% aqueous solution of sodium hydroxide. A blue positive image was obtained.

## EXAMPLE 15

A subbed polyethylene terephthalate film was coated with a solution of 5 g of cresol-formaldehyde resin, type Novolak (prepared analogously to the preparation of Example 9) in 48 g of ethanol, so that upon drying a layer having a thickness of 5 microns was formed. A covering layer consisting of the following ingredients was applied thereto:

8%	aqueous solution of gelatin	1 g
	carbon dispersion as described in Example 1	1 g
5%	aqueous solution of a poly-oxyethylene resin having a melting point of 66°C and a viscosity of 300 cps at 25°C	9 g
	water	36 g
	ethanol	10 g
11.5%	aqueous solution of saponine	1 g

After having been dried, the resulting heat-sensitive material had an optical density (measured by transmission) of 0.86. The material was exposed as described in Example 1. The complete covering layer was removed with running water. Subsequently the material was rinsed for 1 min. in a 0.6% aqueous solution of sodium hydroxide, whereby the exposed areas of the cresol-formaldehyde resin layer dissolve. This can be observed by colouring the freed parts of the substratum of the polyethylene terephthalate film by means of a 1% aqueous solution of a dye e.g. crystal violet. The alkali treated material can be used e.g., as a positive offset printing plate.

## EXAMPLE 16

A paper support weighing 90 g/sq.m. was coated with a solution consisting of:

	water	92 g
	gelatin	6 g
	10% dispersion of black colloidal silver in water	4 g
	11.5% aqueous solution of saponine	1 g
	20% aqueous solution of formaldehyde	1 g

The resulting layer contained 0.27 g of silver per sq.m. and was coated with a covering layer consisting of a solution of 5 g of cresol-formaldehyde resin, type novolak prepared analogously to the preparation in Example 9) in 48 g of ethanol. The dried covering layer was 6 microns in thickness. The material was exposed as described in Example 1, dipped for 45 sec. in a 0.6% aqueous solution of sodium hydroxide, rinsed for a while in water, and dipped for 10 sec. in a bleaching bath comprising 15 g of potassium bromide and 15 g of potassium

hexacyanoferrate(III) per litre of water. A black positive image was obtained since the bleaching only occurred at the exposed areas of the heat-sensitive material, where the heated cresol-formaldehyde resin covering layer was removed by the sodium hydroxide solution.

#### EXAMPLE 17

A subbed polyethylene terephthalate support was coated with a solution comprising:

	ethanol	150 ccs
	poly(N-vinylpyrrolidone)	3 g
	dimethylolmelamine - formaldehyde resin (a 20% aqueous solution has a pH 8.2)	14 g
15	Sudan brown BB (C.I. 12,020)	1 g

The dried heat-sensitive layer was 8 microns in thickness. It was brought in contact with an original and reflex exposed to infrared radiation in a "Secretary" (Trade Mark) apparatus of MMM of Saint Paul, Minnesota (U.S.A.). The parts of the heat-sensitive layer that were heated according to the image areas of the original were removed by rubbing with a plug of wadding soaked with water. A brown negative print was obtained from the original.

#### EXAMPLE 18

A subbed cellulose-triacetate support was covered with a coating composition for a heat-sensitive recording layer from a dispersion consisting of:

35	a 10% solution in ethanol/water (1:9) of polyvinyl alcohol with a degree of hydrolysis of 73-76% (viscosity of a 4% aqueous solution: 7 cps)	300 ccs
40	a 10% aqueous solution of dimethylolurea	200 ccs
	a 1% solution of naphthoquinone - (1,2) - diazide - (2)-5 - sulphonyl fluoride in acetone	100 ccs
45	carbon dispersion as described in Example 1	3 g

The dried heat-sensitive material had an optical density (measured by transmission) of 0.64. The material was exposed as described in Example 1 and rinsed in ethanol. A black positive print was obtained from the original. Using no carbon dispersion in the coating composition no differentiation after exposure and rinsing could be detected.

#### EXAMPLE 19

A subbed polyethylene terephthalate film was coated with a dispersion obtained by ball-milling the following ingredients for 6 hours:

	methylene chloride	88 ccs
	carbon black	0.3 g
	a non-hardenable phenol-formaldehyde resin whose solubility in ethanol increases by heating, sold under the trade mark SUPER - BECKACITE - G 3094 by Reichold Chemie A.G., Hamburg, W.-Germany (melting point: 130°C)	12 g
		60
		65

The dried material had an optical density (measured by transmission) of 0.28.

The material was exposed as described in Example 1. The exposed areas were rubbed away by means of a plug of wadding soaked with ethanol. A grey black copy was obtained from the original.

#### EXAMPLE 20

A subbed polyethylene terephthalate film was coated with a dispersion consisting of:

	a 40% anionic emulsion of a copoly (styrene - N - vinylpyrrolidone) (93/7) in water	30 ccs
	water	70 ccs
	carbon dispersion as described in Example 1	0.3 g
		80

The dried material had an optical density (measured by transmission) of 0.25. The material was exposed as described in Example 1 and rinsed in ethanol. A positive print was obtained from the original.

#### EXAMPLE 21

The following ingredients were ball-milled for 6 hours:

	copoly(butadiene-styrene) (15/85) (a 33.5% solution in xylene has a viscosity of 195 cps at 25°C)	50 g
	2,2 - bis(2 - bromo - 6 - diazo - 2,4 - cyclohexadiene - 4 - yl - 1 - one) - propane	5 g
	carbon black (average particle size: 0.1 microns)	2 g
	methylene chloride	500 ccs
		95
		100

The resulting dispersion was applied to a polyethylene terephthalate support so that upon drying an optical density (measured by transmission) of 0.94 was obtained. The material was exposed as described in Example 1 and rinsed in carbon tetrachloride. A black positive print was obtained from the original. Repeating the whole procedure, using no light-absorbing pigment in the heat-sensitive layer, no differentiation during rinsing could be obtained.

## EXAMPLE 22

The following ingredients were ball-milled for 12 hours:

	crude shellac	10 g
5	FeO·Fe <sub>2</sub> O <sub>3</sub> (average particle size 0.1 $\mu$ )	4 g
	ethanol	60 ccs

The resulting fine dispersion was applied as such to a subbed polyethylene terephthalate film support in such a way that upon drying a layer of 16 microns thickness was obtained. The material was exposed as described in Example 1. The exposed portions were removed by rubbing with a plug of wadding soaked with ethanol. A red-brown positive image was obtained.

## EXAMPLE 23

A subbed polyethylene terephthalate film support was coated with a dispersion comprising:

	non-ionic 38% by weight aqueous dispersion of copoly-(styrene/ethyl acrylate ester) (20/80)	10 ccs
25	water	90 ccs
	carbon dispersion as described in Example 1	0.3 g

The dried heat-sensitive material had an optical density (measured by transmission) of 0.30. It was exposed as described in Example 1 and then rinsed with acetone. A positive copy was obtained from the original.

## EXAMPLE 24

A polyethylene terephthalate support provided with a gelatin-containing subbing layer composition offering more hydrophilic surface properties than the polyethylene terephthalate itself was coated with a solution comprising:

40	ethanol	50 g
	phenol-formaldehyde resin, type Novolak (prepared as described in Example 9)	5 g

The dried heat-sensitive layer was 16 microns in thickness. It was brought in contact with a reversed negative silver image and reflex exposed to infrared radiation in a "Secretary" apparatus of Minnesota Mining and Manufacturing Company, St. Paul, Minn., U.S.A. The parts of the heat-sensitive layer that were heated according to the image areas of the original could be removed by rubbing with a plug of wadding soaked with a 0.6% aqueous solution of sodium hydroxide. After treating the coated side of the film with a lithographic solution containing 5 g of gum arabic and 1 g of phosphoric

acid 85% in 100 ccs of distilled water, a positive offset printing plate was obtained.

## EXAMPLE 25

The following ingredients were ball-milled for 17 hours:

	isopropanol	1000 g
	polyacrylic acid	125 g
	carbon black (average particle size: 0.1 $\mu$ )	31 g
	Crystal Violet (C.I. 42,555)	117 g

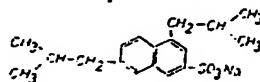
To the resulting dispersion was added a solution of 39 g of poly(1,2-dihydro-2,2,4-trimethylquinoline) in 320 g of isopropanol. The whole was coated on a subbed polyethylene terephthalate film at a ratio of 75 g per sq.m. and dried.

The recording material was then exposed through a silver image line transparency (the silver image side was in contact with the recording layer) by means of a flash lamp having an exposure time of  $8 \cdot 10^{-2}$  sec. The material was irradiated with an energy of 1.03 Wattsecond/cm<sup>2</sup>. The exposed areas were rubbed away by means of a plug of wadding soaked with water. A reversed positive image of the original transparency was obtained. That image was used as a master in hectographic printing whereby several right reading violet copies were obtained.

## EXAMPLE 26

A subbed polyethylene terephthalate film was coated at a ratio of 90 g per sq.m. with a composition consisting of:

	demineralised water	510 ccs
	poly(N-vinylpyrrolidone)	70 g
	dimethylolmelamine - formaldehyde resin whose pH was 8.2 in a 20% aqueous solution	70 g
	Heliogen Grün G.N. Colanyl Teig (a green phthalocyanine pigment dye C.I. 74,260—marketed by Badische Anilin- & Soda-Fabrik A.G., Ludwigshafen a/Rh., W-Germany)	30 g
	5% solution of the compound having the formula:	



in a mixture of ethanol and demineralised water (1:1) 20 ccs

After drying, the heat-sensitive layer was brought into contact with an original and reflex exposed to infrared radiation in a "Secretary" apparatus of Minnesota Mining

and Manufacturing Company, St. Paul, Minn., U.S.A. The parts of the heat-sensitive layer that were heated according to the image areas of the original were removed by rubbing with a plug of wadding soaked with ethanol. A green negative print of the original was obtained.

#### EXAMPLE 27

A subbed cellulose triacetate film was coated at a ratio of 30 g per sq.m., with a composition consisting of:

	demineralised water	770 ccs
	80% aqueous solution of a dimethyl - trimethylolmelaminic-formaldehyde resin	100 g
15	ascorbic acid	20 g
	10% solution of isooctylphenyl polyethylene oxide in demineralised water	70 ccs
20	aqueous carbon black dispersion as described in Example 1	30 g

After drying of the coated layer the recording material was reflex exposed while in contact with an opaque line original by means of an electronic flash-lamp irradiating the recording material with an energy of 0.43 Wattsecond/cm<sup>2</sup>, and having an exposure time of 2.10<sup>-3</sup> sec.

Further the areas of the recording layer corresponding with the white areas of the original were selectively removed by rubbing with a plug of wadding soaked with water. A positive black copy of the original was obtained.

#### EXAMPLE 28

To a solution of 5 g of poly(1,2 - dihydro-2,2,4 - trimethylquinoline) in 30 ccs of a 5% aqueous solution of hydrochloric acid was added a composition consisting of:

	demineralised water	74 ccs
40	polyethylene glycol having an average molecular weight of 200	5 g
45	aqueous carbon black dispersion as described in Example 1	4 g

The resulting dispersion (pH 2) was coated on a subbed cellulose triacetate film in such a way that upon drying the resulting material had an optical density (measured by transmission) of 1.36.

The recording material was exposed through a halftone transparency by means of a flash lamp having an exposure time of 2.10<sup>-3</sup> sec. and irradiating the material with an energy of 0.51 Wattsecond/cm<sup>2</sup>. The exposed areas were then removed by rubbing with a plug of wadding soaked with water. A black copy of the original was obtained.

#### EXAMPLE 29

The following ingredients were ball-milled for 6 hours:

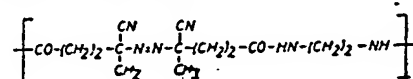
	ethanol	74 g	
	18.5% solution of polyacrylic acid in isopropanol	20 g	
	carbon black	2 g	65
	2,4-dihydroxy-benzophenone	4 g	

The resulting dispersion was coated on a subbed polyethylene terephthalate film in such a way that upon drying the resulting material had an optical density (measured by transmission) of 5.50. The recording material was exposed as described in Example 1. The exposed areas were then removed by rubbing with a plug of wadding soaked with water. A black copy of the original was obtained.

#### EXAMPLE 30

The following ingredients were ball-milled for 6 hours:

	methylene chloride	50 g	
	carbon black (average particle size: 0.1 microns)	1 g	80
	a polyamide containing the following recurring units:		



prepared according to a method as described in Die Makromolekulare Chemie, 103 (1967) p. 301-303

5 g

The resulting dispersion was coated onto a subbed polyethylene terephthalate film in such a way that after drying the resulting material had an optical density (measured by transmission) of 0.80. The recording material was exposed as described in Example 1 and the exposed portions were removed by rubbing with a plug of wadding soaked with a 2% aqueous solution of trisodium ortho phosphate. A greyish black positive image of the original was obtained.

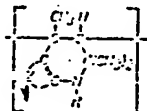
#### WHAT WE CLAIM IS:—

1. An information-recording method wherein a recording material is used comprising a heat-sensitive recording layer of a composition such that the solubility of any given area of the layer in a given solvent (to be used in the method) can be increased by heating that area of the layer, wherein the said layer is information-wise heated to produce a record of the information in terms of a difference in the solubilities in the said solvent of different areas of the recording layer, and wherein the whole layer is then contacted with such solvent to cause the por-



tions of the recording layer which are soluble or most soluble in such solvent to be removed or penetrated by such solvent, the said method being characterised in that the said recording layer is wholly or mainly composed of one or more heat-sensitive polymeric compounds or compositions identified in the following list:

- (1) galactomannan;
- (2) a hydroxypropylmethyl-cellulose;
- (3) a slightly hardened methylol-melamine resin or a slightly hardened wholly or partly etherified methylol-melamine resin of the water-soluble type;
- (4) a resorcinol-formaldehyde resin which is soluble in ethanol or in a mixture of water and ethanol and which becomes soluble in water alone by heating
- (5) a composition containing a water-soluble polyvinyl alcohol mixed with a compound containing (a) reactive carbonyl group(s)
- (6) a composition which becomes water-soluble or more water-soluble on heating and comprises an acidic compound and a water-insoluble polymer containing a basic nitrogen-containing heterocyclic nucleus of the type present in the following recurring unit:



wherein:

Z represents the necessary atoms to complete a substituted or unsubstituted aromatic nucleus, and

R represents hydrogen or a group that maintains the basic properties of the nitrogen atom to which it is attached,

- (7) a reaction product of (a) a water-soluble polymer or copolymer of an  $\alpha,\beta$ -ethylenically unsaturated compound containing at least one carboxylic acid group and (b) a reactive compound, such product being one which is less soluble in water than the  $\alpha,\beta$ -ethylenically unsaturated compound but which on being heated dissociates to form a composition which is more soluble in water than said reaction product.
- (8) a cresol-formaldehyde resin of the novolak type
- (9) a phenol-formaldehyde resin of the novolak type
- (10) a polymer containing an azo group linked through a carbon atom to a nitrile group

- (11) poly-N-vinylpyrrolidone
- (12) crude and/or bleached shellac
- (13) poly(1,2 - dihydro - 2,2,4 - trimethyl-quinoline)
- (14) poly-N-vinylpyrrolidone in admixture with a water-soluble melamine-formaldehyde resin;
- (15) a composition containing polyvinyl alcohol or a partially hydrolyzed polyvinyl acetate mainly containing vinyl alcohol units, mixed with a quinonediazide compound and an aldehyde or latent aldehyde;
- (16) a copoly(styrene / N-vinylpyrrolidone) which has been used as a latex in forming the recording layer and which undergoes an increase in solubility in ethanol or another  $C_1$   $C_2$  alkanol on being heated.
- (17) a copoly(styrene/acrylate ester) which has been used as a latex in forming the recording layer and which undergoes an increase in solubility in acetone on being heated.
- (18) a composition containing a copoly-(butadiene/styrene) and an o-quinonediazide compound.

2. A method according to claim 1, wherein the recording layer is black or coloured and after the information-wise heating of the recording layer the soluble or the most soluble portions thereof are removed by the solvent treatment so as to leave a black or coloured record.

3. A method according to claim 1 or 2, wherein the recording layer contains at least one of the compounds or compositions numbered 1 to 7, and wherein after the information-wise heating the heated portions of the recording layer are removed by means of water.

4. A method according to claim 1 or 2, wherein the recording layer contains at least one of the compounds or compositions numbered 8 to 12, and wherein after the image-wise heating the heated portions of the recording layer are removed by means of an aqueous alkaline liquid.

5. A method according to claim 1 or 2, wherein the recording layer contains at least one of the compounds or compositions numbered 12 to 16, and wherein after the image-wise heating the heated portions of the recording layer are removed by means of a  $C_1$ - $C_4$  alkanol.

6. A method according to claim 1 or 2, wherein the recording layer contains at least one of the compounds 16 or 17 and wherein after the image-wise heating is treated with ketone containing two  $C_1$ - $C_4$  alkyl groups linked to the carbonyl group.

7. A method according to claim 1 or 2, wherein the recording layer contains the composition 18, and wherein after the image-wise heating the heated portions of the re-



recording layer are removed by means of a chlorinated aliphatic hydrocarbon compound.

- 5 8. A method according to any preceding claim, wherein the recording layer contains a distributed coloured substance or substances which is or are capable of absorbing infra-red radiation and/or visible or ultraviolet light and wherein the said layer is information-wise heated by information-wise exposing such layer to radiation which is absorbed by such substance(s) so that the heat is generated within such layer by radiation absorption.

- 10 9. A method according to claim 8, wherein the recording layer has an optical density of more than 0.25.

- 15 10. A method according to claim 8 or 9, wherein the recording layer incorporates finely divided carbon particles, particles of a heavy metal, or an oxide or a sulphide of a said metal as substance which absorbs said radiation.

- 20 11. A method according to any of claims 8 to 10, wherein the exposure is a short-duration high-intensity image-wise exposure.

- 25 12. A method according to claim 11, wherein the exposure lasts no longer than  $10^{-1}$  seconds.

- 30 13. A method according to claim 12, wherein the exposure is carried out by means of a flash lamp emitting a larger amount of visible light than of infra-red radiation.

- 35 14. A method according to any of claims 8 to 13, wherein the recording layer contains a said distributed substance which can be bleached in the heated portions.

- 40 15. A method according to any of claims 1 to 7, wherein the information-wise heating is effected by heating the image markings of a graphic original located in contact with the recording material.

- 45 16. A method according to any preceding claim, wherein the recording layer contains a dye and following the information-wise heating, the soluble or most soluble portions of the recording layer are removed and the recording material is then used as a master in spirit duplicating by means of a printing liquid which dissolves such dye.

- 50 17. A method according to claim 16, wherein the said soluble or most soluble portions of the recording layer are removed by washing them away in an apparatus according to the United Kingdom Patent Application No. 25646/67 (Spec. No. 1,212,994).

- 55 18. A method according to any preceding claim, wherein the recording layer is carried directly or through a subjacent layer, by a support and wherein after the information-wise heating of the recording layer, the soluble or most soluble portions thereof are removed and the said support or subjacent layer is etched.

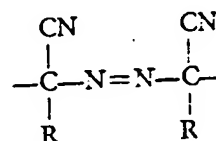
- 60 19. A method according to claim 3 or any

of claims 8 to 18 insofar as such claim is dependent on claim 3, wherein said recording layer contains a composition which is numbered (6) in claim 1 and in which the acidic compound is a polymer or copolymer of an  $\alpha,\beta$ -ethylenically unsaturated compound containing a carboxylic or sulphonic acid group.

- 70 20. A method according to claim 3 or any of claims 8 to 18 insofar as such claim is dependent on claim 3, wherein said recording layer contains a composition which is numbered (6) in claim 1 and in which the said water-insoluble polymer is poly(1,2-dihydro-2,2,4-trimethylquinoline).

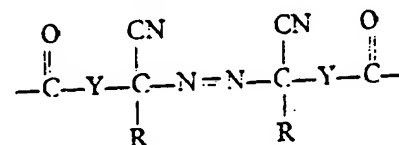
- 80 21. A method according to claim 3 or any of claims 8 to 18 insofar as such claim is dependent on claim 3, wherein said recording layer contains a composition which is numbered (6) in claim 1 and in which the acidic compound is present in a weight ratio of 20-400% with respect to the water-insoluble polymer.

- 85 22. A method according to claim 4 or any of claims 8 to 18 insofar as such claim is dependent on claim 4, wherein said recording layer contains a compound which is numbered (10) in claim 1 and which is a polymer comprising groups of the following structure:



wherein R represents a lower alkyl group.

23. A method according to claim 22, wherein such polymer is a polyester or polyamide containing the following structural group in its recurring units:



wherein R represents a lower alkyl group, and Y represents a bivalent hydrocarbon radical.

24. A method according to claim 5 or any of claims 8 to 18 insofar as such claim is dependent on claim 5, wherein said recording layer contains a composition which is numbered (15) in claim 1 and which includes a quinone-diazide compound as described in United Kingdom Patent Application No. 8728/66 (Spec. No. 1,136,544).

25. A method according to claim 5 or any of claims 8 to 18 insofar as such claim is dependent on claim 5, wherein said recording layer contains a composition which is numbered (15) in claim 1 and which includes

formaldehyde or a latent aldehyde which splits off formaldehyde on heating.

26. A method according to claim 5 or any of claims 8 to 18 insofar as such claim is dependent on claim 5, wherein said recording layer contains a composition which is numbered (15) in claim 1 and which includes naphtho - quinone - 1,2 - diazide(2) - 5-sulphonyl chloride or naphtho - quinone - 1,2-diazide(2) - 4 - sulphonyl chloride.

27. A method according to claim 5 or any of claims 8 to 18 insofar as such claim is dependent on claim 5, wherein the recording layer contains a composition which is

numbered (15) in claim 1 and which includes an ortho-quinone diazide compound as described in United Kingdom Patent Specification No. 1,116,737.

28. An information recording method substantially according to any of the Examples herein.

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